PB90-201799

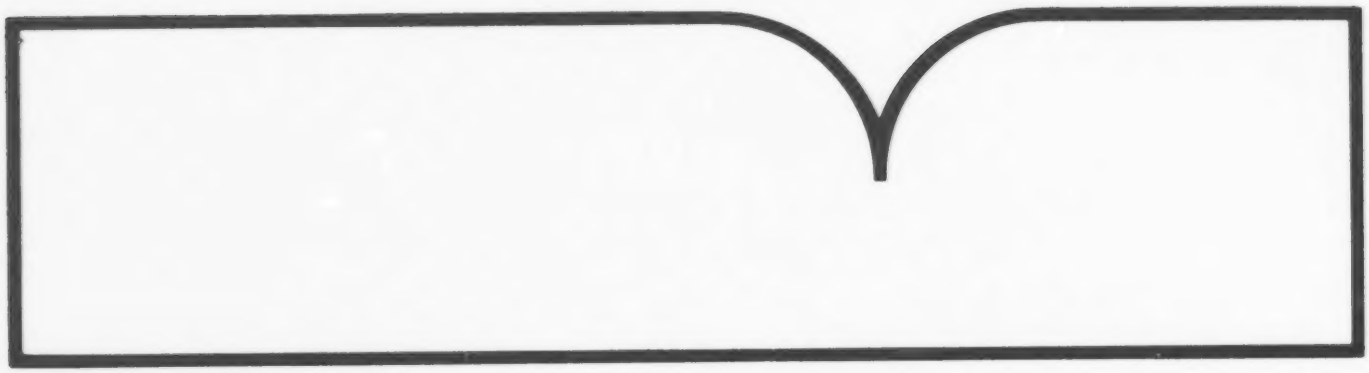
Preliminary Exposure Study to Determine the Effects of Acid Deposition on Coated Steel Substrates

Johns Hopkins Univ., Baltimore, MD

Prepared for:

Environmental Protection Agency, Research Triangle Park, NC

1 Apr 90



U.S. Department of Commerce
National Technical Information Service
NTIS

PB90-201799

EPA/600/3-90/032
April 1990

PRELIMINARY EXPOSURE STUDY TO DETERMINE THE EFFECTS OF ACID DEPOSITION ON COATED STEEL SUBSTRATES

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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	PB 90 201799/AS
EPA/600/3-90/032		

4. TITLE AND SUBTITLE	5. REPORT DATE
PRELIMINARY EXPOSURE STUDY TO DETERMINE THE EFFECTS OF ACID DEPOSITION ON COATED STEEL SUBSTRATES	April 1990
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
P. Moran, et. al. (see title page for other authors)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
The Johns Hopkins University Department of Materials Science and Engineering Baltimore, MD 21218 (See title page for other affiliations)	N104/G/02/15 - 6I (FY-90)
	11. CONTRACT/GRANT NO.
	CR 814347-01
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Atmospheric Research & Exposure Assessment Lab - RTP Office of Research and Development U. S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	Final
	14. SPONSORING AGENCY CODE
	EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report describes the progress that has been made within the Coatings Effect Research Program that the Environmental Protection Agency conducts for Task Group VII within the National Acidic Precipitation Assessment Program. This project involves the evaluation of the effects of acidic pollutants on painted metal substrates. The project examined a commercially available alkyd paint/primer system applied to a low carbon steel substrate exposed under a variety of simulated acidic conditions to determine the micro/macro effects of such exposure. The techniques that were identified as those most sensitive and applicable during the study include tensile adhesion testing, electrochemical impedance spectroscopy (EIS), and x-ray photoelectron spectroscopy (XPS). A novel electrochemical monitor was developed during this program that allowed the continual monitoring of coating degradation during chamber exposure. It was further found that a good correlation existed between tensile adhesion strength measurements and electrochemical impedance parameters. The program determined that the rate of degradation of the alkyd painted steel coupons was accelerated in the presence of SO_4. This effect was most pronounced on samples that contained defects (scribes), that were allowed to form condensed (dew) during the exposure period and that had a horizontal orientation during exposure.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	36
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

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ABSTRACT

This report describes the progress that has been made within the Coatings Effect Research Program that the Environmental Protection Agency (EPA) conducts for Task Group VII within the National Acidic Precipitation Assessment Program (NAPAP). This project involves the evaluation of the effects of acidic pollutants on painted metal substrates. The project examined a commercially available alkyd paint/primer system applied to a low carbon (ASTM A569 CQ) steel substrate exposed under a variety of simulated acidic conditions to determine the micro/macro effects of such exposure. The original objectives of this research program which was terminated by EPA after year two of the planned four (along with all EPA programs dealing with the effects of acidic deposition on materials), were as follows:

1) Identify the analytical methods which are most appropriate to identify and/or quantify changes in chemical (structure, bonding, and content) or physical (adhesive, mechanical, and electrochemical) properties of the coatings as a result of exposure to field and/or laboratory conditions.

2) Determine the contributions of atmospheric pollutants/conditions [SO_2, NO_x, O_3,(at ppm levels); UV-radiation; etc.] to degradation of coatings.

3) Evaluate the relationship between the micro-damage identified in the laboratory and field studies and macro-damage (blistering, peeling, undercutting, rusting, cracking, fading, etc.) leading to coating/substrate failure.

This report details the results obtained in the program which include completion of objective one and efforts toward completion of objective two. The results focus on the screening and development of sensitive analytical techniques and the use of these techniques to investigate effects of SO_2 on alkyd painted steel coupons during laboratory exposure. Both immersion and chamber exposures were conducted. The techniques that were identified as those most sensitive and applicable during the study include tensile adhesion testing, electrochemical impedance spectroscopy (EIS), and x-ray photoelectron spectroscopy (XPS).

A novel electrochemical monitor was developed during this program that allowed the continual monitoring of coating degradation during chamber exposure. It was further found that a good correlation existed between tensile adhesion strength measurements and electrochemical impedance parameters. This demonstrates that the non-destructive EIS measurements are a sensitive and true measure to evaluate extent of degradation. The program determined that the rate of degradation of the alkyd painted steel coupons was accelerated in the presence of SO_2; this effect was most pronounced on samples that contained defects (scribes), were dew cycled (were allowed to form condensed dew during the exposure period), and had a horizontal orientation during exposure.

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SECTION 1

SUMMARY OF MICRO-MACRO DAMAGE

A summary of the micro-macro damages of coated-steel substrate systems that were observed during exposures of a commercially available alkyd maintenance coating system on ASTM A 569 CQ low carbon steel to conditions simulating acidic deposition are as follows:

A) Loss of Adhesion

Exposure to 1 ppm SO_2, in a high humidity environment accelerates loss of adhesion between the paint/primer and metal substrate. There appears to be no significant loss in paint system cohesive strength.

In contrast, in sulfurous acid immersion paint cohesive strength decreases prior to loss of coating adhesion at the interface.

B) Adsorption/Absorption of Sulfur

For chamber samples exposed to 1ppm SO_2 certain distinct differences in the adsorption and uptake of sulfur were witnessed dependant on the specific exposure conditions or the pre-exposure history of the samples as detailed below:

*Nominally dry specimens
-high S surface adsorption that is enhanced by pre-exposure to ultra-violet radiation (UV). No orientation dependence

*Dew-exposed specimens
-low S surface adsorption for specimens allowing dew runoff (mounted vertically);
varying S surface adsorption (see C, below) for specimens retaining dew (mounted horizontally).

For immersion samples, exposed to either distilled water or to pH 3 sulfuric, nitric, or sulfurous acids:

*In sulfurous acid S penetrates through topcoat and primer.
*In sulfuric acid no appreciable uptake (absorption) of S was detected.

C) Discoloration

On dew exposed horizontal samples brown discolored areas appeared 1-2 days after removal from chamber (exposed to 1 ppm SO_2, 95% RH). Discolored regions extended partially through the topcoat and exhibited high S concentrations.

White regions adjacent to and below discolored spots exhibited much lower concentrations of S.

D) Electrical Properties

EIS data indicated a decrease in the near DC impedance (impedance at ~5-20 mHz) as a function of exposure time to 1ppm SO_2, 95% RH, indicating coating degradation. Control exposures have verified that this effect is enhanced over that of exposure under nominally identical conditions in the absence of SO_2. The near DC impedance (impedance at ~5-20mHz) is approximately 1-2 orders of magnitude lower in the presence of SO_2 than under nominally identical conditions in the absence of SO_2.

E) Blistering

During chamber exposure blisters occurred only on the thinnest samples (120-170 μm) that were exposed to 1ppm SO_2,95% RH. Blistering did not occur during a control exposure of samples of comparable thickness and thus appeared to be SO_2 induced or related.

Immersion exposed samples in sulfuric, nitric, sulfurous and distilled water each exhibited blistering after a few weeks of exposure. The blistering appeared to be caused by permeation of water through the film and was not dependant on the specific exposure condition.

F) Effects of Defects

Specimens which were chamber exposed to 1ppm SO_2, 95% RH that had been scribed according to ASTM D-1654 exhibited considerable rusting and blistering of the paint coating adjacent to scribed areas. This effect was most severe in samples that were dew cycled and oriented horizontally during exposure. Scribed samples exposed during the control run exhibit only light rusting in the area of the scribe and do not show any signs of blistering.

SECTION 2

INTRODUCTION

The Atmospheric Research and Exposure Laboratory (AREAL) of the Environmental Protection Agency (EPA) has conducted a program entitled, Effects of Acid Deposition on Materials, that was planned by Task Group VII, Effects on Materials and Cultural Resources. This Task Group is one of several groups that conducted research within the National Acid Precipitation Assessment Program (NAPAP). Within Task Group VII, the EPA has the responsibility for studying effects on materials of construction whereas the National Park Service and U.S. Geological Survey studied cultural materials. One of the primary missions of Task Group VII was to provide NAPAP and EPA with scientific data on the cause and effect relationships (damage function models) of acid deposition on man-made and naturally occurring materials. These models are to be used by NAPAP to evaluate the economic loss associated with acid deposition damage to materials. Because of their economic importance and susceptibility to acid deposition, exterior coatings were one of the materials that Task Group VII and the EPA were interested in studying.

Before beginning this study of exterior coatings, U.S. EPA held a workshop to review a planning document entitled "Research Plan for Determining the Effects of Acid Deposition on Exterior Coatings." The plan was approved on January 1987. In addition to this document, the EPA had prepared an internal report entitled "Strategy and Documentation for Conducting Research on the Effects of Acid Deposition on Coating-Substrate Systems: The Data Quality Objective Process" that supplements the Research Plan and provided guidance to researchers who were conducting effects research on coating-substrate systems (1-2). These two documents provided the cornerstone for the research on the micro-macro damage of acidic deposition that was conducted by the EPA.

This report reviews the progress that was made under Task 3 of the research plan. Task 3 sought to develop and select analytical techniques that are appropriate to identify early micro-macro failure processes associated with acidic deposition on coated steel substrate systems and to use these techniques to evaluate such damage. Appropriate analytical techniques would be those that model critical failures occurring in the field. According to a recent report by Lipfert (3) the primary types of paint failures that result in maintenance repainting include peeling, blistering, and cracking. For this reason the candidate techniques that we included in our preliminary screening of analytical techniques were those that would evaluate changes in the painted steel coupons that would lead to such macroscopic failures. Those determined to be the most appropriate for our painted steel system include tensile adhesion testing, electrochemical impedance spectroscopy, and surface analytical techniques.

This text discusses data obtained within the two year program, with specific emphasis on the last 12 months of the program. Additional information on the initial year of the program can be found in a report entitled "Analytical Techniques for Assessing the Effects of Acid Deposition on Painted Steel Substrates" (EPA/600/S3-88/045) available from NTIS(4). Supplemental information regarding more recent studies has also been previously published (5-7). Year one of the program involved completion of a series of preliminary exposure studies to enable screening of a variety of analytical techniques and to determine those that are the most appropriate for the early detection of coating degradation. The recent focus of the program involved the movement to more refined types of exposures i.e. controlled atmosphere in an environmental chamber and the use of those analytical techniques deemed most appropriate in year one to examine the incremental effects of acid deposition on painted metal substrates.

SECTION 3

TECHNICAL APPROACH

The first year of this program involved the completion of four primary tasks: the design and construction of an environmental test chamber, the selection of an initial coating system for study and the development of a method for accelerated cure of the system, preliminary sample exposures (primarily via immersion), and technique screening. The second year of the program involved the use of the most promising analytical techniques (identified in year one) in refined types of exposures to evaluate the damage to painted steel substrates exposed to acidic environments. These techniques included surface analytical [x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive x-ray microscopy (ED-XRM)], and electrochemical [electrochemical impedance spectroscopy (EIS)], The basis of our technical approach throughout the program is summarized briefly in this report.

A) Environmental Exposure Chamber

The environmental test chamber is a custom desinged chamber composed of a 4" diameter, 2 ft. long sample compartment which can accommodate up to 78 1" x 1" x 1/16" painted steel coupons mounted flush to the chamber wall. It is capable of controlled introduction of pollutants and regulation of conditions of temperature and relative humidity. Since flow rates in the chamber are not sufficient to insure turbulent flow, baffles have been incorporated between sample sections to promote mixing and minimize the development of a boundary layer. The inside walls of the chamber are quartz, and the remainder of the system that is exposed to the gas is teflon. The environmental exposure system is monitored and controlled using a computer, to collect the data and to control the 60 l/min mass flow controllers (wet stream) and the sample heater/chiller unit, which regulates the sample temperature. A schematic of the environmental exposure chamber is shown in Fig. 1. Initial sample exposures in the chamber began on June 28, 1988.

B) Sample Preparation

All test panels made from steel (ASTM A 569 CQ). Coupons of two different sizes (4" x 6" x 1/16" and 1" x 1" x 1/16") were used in these studies. All sample coupons were prepared according to the following procedures. The coupons were solvent degreased and grit-blasted to a white metal finish. After discussions with AREAL, a commercially available alkyd primer/topcoat paint system, typically used for steel storage tanks, was selected for these studies. The primer/top coat system, which does not contain sulfur, was spray applied onto the clean coupons. The front side of the coupons was coated with a layer of primer followed by a single or double layer of topcoat. The back side of the coupons was coated with one layer of primer and two layers of topcoat. The edges were coated with primer and brush coated twice with topcoat. Free-standing paint films (200-250μm) were prepared by pouring paint of adequate viscosity onto a teflon plate and spreading it out using a doctor blade. The free-films were allowed to dry on the plate overnight at room temperature under standard laboratory conditions. All the coupons and films were then oven cured in air at 100°C for 1 hr, after a gradual heat up rate (taking approx. 70 min.) from room temperature to 100°C. Specimens had dry film thicknesses of either 120-170μm (later studies) or 250-300μm (immersion studies and early chamber studies). Some specimens contained a scribe extending diagonally across the specimen according to ASTM D-1654.

Nearly-fully cured, reproducibly prepared, samples are essential for interpretation of results. A series of tests were performed to ensure such factors. Differential scanning calorimetry (DSC) thermograms were generated for paint films scraped off their substrate that had undergone different cure times and temperatures. Films cured at room temperature (48 hours) and at 70°C (2 hours) showed a characteristic exotherm with a peak at approximately 100°C associated with an incomplete cure. When the same films were re-run after they had cooled, the exotherm disappeared indicating heating in the DSC had fully cured them. Films cured at 100°C for at least 1 hour did not exhibit any exotherm. Additional films were examined using a thermogravimetric analyzer. Films cured at room temperature for six days showed constant weight loss as solvents evolved during cure. In contrast, films cured at 100°C for 1 hour showed no weight loss.

Tensile adhesion tests for specimens cured at 100°C for various times (30 min --> 8 hours) and specimens cured at 100°C for 1 hour and stored at room temperature for a minimum of three weeks and for up to six months showed high cohesive strengths (800-1000 psi) with failures, occurring within the paint system. No significant change was observed during the longer cure or storage time. It was determined that it was necessary to wait 3 weeks between initial sample preparation/curing and sample use to insure high cohesive strengths. All samples were stored for a minimum of three weeks prior to usage.

A series of samples cured at 100°C for 1 hour were also immersed in pH 3 H_2SO_4 and examined via EIS as a function of exposure time. EIS data for all samples were nearly identical indicating good sample:sample reproducibility. Initial near DC impedance values for samples containing two layers of topcoat were $\sim 10^{11}$ ohms.

C) Promising Analytical Techniques

A number of analytical techniques have been identified which appear promising for the early detection of coating degradation in an acidic deposition environment. These techniques have been applied to characterize degradation of chamber-exposed and aqueous-immersed painted steel coupons. Each of the ex-situ and in-situ techniques which have been identified as promising are detailed below indicating the key information which can be obtained using the technique.

Weight gain/loss measurements are the simplest of the measurements completed on all chamber exposed specimens to indicate the rate of uptake of pollutants and/or water.

Tensile adhesion tests measure either the cohesive strength (paint or primer) or the adhesive strength (topcoat/primer or primer/substrate) whichever is less. Examination of the failure surfaces (visually or, in certain cases, by XPS) identifies the weakest link of the system while the strength value gives an indication of the degree of degradation. Tensile adhesion testing is performed using a pneumatic adhesion tensile testing instrument (SEMicro, Rockville, MD). The test is schematically illustrated in Fig. 2. A 1.25 cm diameter Al stud is bonded to the paint surface with a two part epoxy resin (3M, #1838, room temperature cure) shortly after removal from the chamber. The bonding area is defined with a Teflon ring and the epoxy is allowed to cure for 48 hours. The Teflon ring is replaced by a jig to prevent the specimen from flexing and a pneumatic piston is attached to the stud. Increasing tension is then applied to the stud until separation occurs. The loci of failure were determined visually in most cases. If there was any ambiguity, XPS was used to clarify the matter. Because of some variation from specimen to specimen, at least three coupons for each exposure condition were tested; the results presented are averages.

XPS has the potential for being one of the most sensitive ex-situ means of detecting early degradation because of its surface sensitivity. It has been used to measure acidic deposition onto the coating surface and to identify changes in the surface chemistry as a function of exposure in the environmental chamber and in the field. The XPS measurements were performed using a Surface Science Instruments Model SSX 100-03 spectrometer, consisting of a monochromatized Al K alpha x-ray source and a hemispherical electron energy analyzer with multichannel detection. The x-ray source was focused to a spot size of 600μm. The samples were isolated from ground during analysis; the surface charge was neutralized by a wire grid just above the sample surface and low-energy electron bombardment. Survey spectra were used for the initial qualitative analysis and high-resolution spectra [with a full width a half maximum (FWHM) of the Au $4f_{7/2}$ = 1.1 eV] of the appropriate photoelectron peaks were used for quantitative analysis and chemical state determination.

SEM together with cross-sectional ED-XRM allows indiffusion of the deposited material and outdiffusion or leaching of coating constituents to be measured. It provides a "snap shot" of the distribution of material at a given time and allows the progress of material transport to be charted for the different exposures. ED-XRM measurements were performed using a JEOL 100 CX STEM with a Tracor Northern TN-4000 EDS attachment.

EIS has been used to examine the electrochemical properties of the paint/substrate system. Other investigators have recently shown good correlations for EIS parameters in assessing coating degradation for

immersion in seawater, soil, and commercial products(8-13); we have developed an atmospheric electrochemical monitor (ATMEIS) for conducting these measurements during atmospheric exposures. EIS was the only analytical method, utilized within this program, that was appropriate for in-situ testing in the atmospheric exposure chamber. Chamber exposed samples were monitored by EIS throughout the exposure time to determine the relative effects on coating degradation. The fact that samples remain in the chamber throughout such studies makes EIS invaluable in determination of the onset and extent of degradation and establishing the relative contributions from each pollutant/condition. EIS data have been collected using an EG&G PAR 273 Potentiostat and a 5208 EC lockin amplifier over a frequency range of 5 mHz to 100 kHz. Low frequency data were collected using a fast-fourier transform method to apply the voltage signal and collect the data. All experiments were performed using the M378 software commercially available from PAR.

Thermal characteristics of the paint films were measured using differential scanning calorimetry, (DSC), and thermogravimetric analysis (TGA). These properties allowed us to determine the conditions under which the paint film cures and then becomes embrittled and/or loses strength during exposure thus leading to macro-damage. DSC measurements were made using a Mettler Instruments DSC-30 calorimeter. TGA measurements were made using a Dupont Instruments 951 TGA.

SECTION 4

RESULTS AND DISCUSSION

A) Initial Immersion Exposures

Painted steel coupons were immersed in one of four different environments: aerated solutions of either nitric acid, sulfuric acid or distilled water, or a deaerated solution of sulfurous acid. The acidic solutions were maintained at pH 3 throughout the exposure time. Free standing paint films were also exposed to each solution. Results of each of the specific analytical techniques chosen to examine the degradation of these sample coupons are detailed briefly below. It should be emphasized that all immersion studies, unless specifically noted, were conducted on samples containing a single layer of topcoat on the front side of the sample and a double layer of topcoat on the back and edges of the sample.

After two weeks of exposure, the edges of the panels in the nitric and sulfuric acid baths began to show very slight rust stains. The edges of the panels exposed to the sulfurous acid solution did not appear to have been attacked, however small blisters began to form on the surface. At later exposure times each of the exposed sample coupons exhibited blisters which appeared to increase in number with time. The blisters were filled with an aqueous solution whose pH is approximately 8. The primary cause of the blistering was felt to be the uptake of water through the coating.

XPS measurements of the organic coatings on exposed samples indicated a small adsorption of S (0.2- 0.6 at. %) as a sulfate and N (2-4 at. %) as an amine on all samples, including those immersed only in distilled water. The source of the S and N is unknown. For samples exposed to water, sulfurous and nitric acids, a small amount of Zn (approx. 0.2 at. %) was also observed, most likely originating from the primer.

ED-XRM line profiles were made across primer/paint cross-sections for as-prepared samples and for samples exposed for 1, 4 and 8 weeks. Samples exposed to water, sulfuric and nitric acids exhibited no indiffusion or leaching of material (elements with $Z > Na$). In contrast, samples exposed to sulfurous acid exhibited an indiffusion of S through the paint and primer and a leaching of primer constituents starting after 1 week of exposure. The comparison of the ED-XRM line profiles and the XPS measurements suggests that the S from the sulfurous acid penetrates the paint and primer films readily and does not accumulate at the intact paint-electrolyte interface.

EIS was also used extensively to characterize immersed samples throughout the exposure time in each of the three acids. From initial impedance values, 5 hours after exposure, evidence of pinholes was apparent. EIS data throughout the exposure period were dominated by the presence of preexisting pinholes, predominately located at the edges of the samples. A cell which does not expose the edges of the sample to solution was subsequently used for EIS analyses of immersed specimens to avoid the contribution of the pinhole defects. Samples exposed in this cell exhibited very high impedance values (10^{10} ohms cm^2) a few hours after exposure, and did not show evidence for appreciable defects until 1-2 weeks after exposure. These data confirmed that defects are largely localized on the edges of the samples.

A primary goal of the initial immersion studies was the screening and development of techniques that would be appropriate for chamber and field exposure studies. Since conventional EIS studies in immersion environments were appropriate for the evaluation of these painted metal coupons, efforts to modify the EIS methods to enable EIS measurements to be made during chamber studies were initiated. EIS is a desirable technique to monitor paint degradation since it is quite sensitive and essentially non-destructive. Although EIS has been used by several investigators to assess coating degradation in immersion environments, to date, it has not been adequately applied to characterization of degradation in atmospheric exposure. Our efforts involved the design and testing of an atmospheric electrochemical monitor (ATMEIS) to be used to generate EIS data during atmospheric exposure. The ATMEIS monitor consists of a painted steel coupon upon which a gold electrode (covering less than 10% of the front surface of the sample coupon) is electron-beam deposited. The impedance of the substrate/coating system is determined in a two electrode measurement using the steel substrate as one electrode and the electron-beam-deposited gold as the second electrode. The monitor can be used, therefore, in the absence of a remote reference or counter electrode.

The monitor was developed to assess the degradation of organic coatings in atmospheric exposures simulating acid deposition.

ATMEIS specimens were prepared by using electron beam evaporation to deposit a layer of gold (200 nm thick) onto the surface of the coated steel specimens. A photoresist was then spun down on the surface and cured at 80°C for 25 min. The photoresist was then exposed to UV (320 nm, 20 sec.) through a mask (18mW/cm^2, positive) containing the desired electrode pattern. The remaining gold, not covered by the photoresist was then etched with KI/I_2 (30 sec). An O_2 plasma was used to strip the photoresist resulting in the final coupon. Figure 3 shows a picture of the ATMEIS monitor mounted for chamber exposure. In immersion exposure only the central portion (defined by the gold grid) of the 2.54 x 2.54 cm coupon would be exposed to solution. The grid consists of a series of lines of gold which are 0.48 mm wide separated by 1.82 mm. The outer dimensions of the central grid (excluding bonding pads) are 13 x 13 mm. The bonding pads are 1.5 x 1.5 mm and are attached to the central grid by 0.48 mm x 5 mm lines of gold. Electrical lead wires were attached at the bonding pads on the gold electrode using silver paint.

The monitor relies on the assumption that the impedance of the interface of the deposited electrode lying on the surface of the coating is low relative to the impedance of the coating and the steel-coating interface; an assumption which has been verified as will be discussed. This enables a two electrode measurement rather than a conventional three electrode measurement to be completed. The two electrode approach is valid, because placement of the deposited electrode at the surface of the coating enables its entire interface with the coating to be wetted and utilized, resulting in a low interfacial impedance relative to the coating or the steel-coating interface. The primary value of this monitor is that it has the potential of being used for completely in-situ monitoring of atmospheric or vapor phase coating deterioration on a real-time basis and/or on real structures. Such a method is currently unavailable.

Although the ATMEIS monitor was designed to be used for atmospheric monitoring of coating degradation, preliminary evaluation and validation of the monitor was conducted using immersion exposures. Results from exposures for time periods up to several months demonstrate that the EIS data are essentially identical regardless of whether 1) remote reference and counter electrodes are used, 2) the gold electrode is used as the reference/counter combination with the sample in the aqueous acid electrolyte, or 3) the gold electrode is used as the reference/counter combination with the sample removed from the electrolyte, in air. Fig 4 shows the EIS data, plotted in the Bode magnitude format, for a sample exposed via immersion for one day, and two weeks to pH 3 H_2SO_4 collected using methods one and three detailed above. EIS data which were collected using the gold electrode were identical to those which would be obtained using remote electrodes for the same sample.

In addition, the ATMEIS monitor has shown behavior which is nearly identical to that of an as-prepared sample (conventionally coated without a sputter coated gold electrode) for equivalent exposure times. Within the error associated with sample to sample variation and measurement constraints, there is no significant difference in the behavior of samples with or without the monitor. Thus, the presence of the gold electrode on the sample surface does not appear to effect the normal chemistry/degradation process of the coated metal sample. Further information regarding the preliminary evaluation of the ATMEIS monitor has been previously detailed (5-6).

Tensile adhesion tests were used to measure the cohesive/adhesive strength of the paint system as a function of time in each exposure environment. Studs were bonded to the painted steel prior to and/ or following exposure and the force required to separate the steel and the paint was measured. The failure type and locus of failure in the unexposed coupons was cohesive in the primer. After one week exposure, no change in the tensile strength was noted for the water, nitric, and sulfuric acid-exposed samples and failure continued to be cohesive in the primer. Some decrease in strength (approx. 30%) was seen for the sulfurous acid-exposed samples and failure was partially cohesive in the primer and partially cohesive in the paint with the strength being inversely correlated with fraction of paint failure. The nitric and sulfuric acid-exposed specimens retained their strength at 4 weeks immersion, but lost most of it by 8 weeks. The water and sulfurous acid-exposed specimens lost their tensile strength by 4 weeks. In each case, strength was dependant on the time from removal of specimens from immersion to time of measurement, the lowest strength being seen if the measurement was completed shortly after removal from exposure. Tests performed a few days after removal from immersion indicated a partial regaining of strength. Presumably this time dependance

was a result of the paint/primer system losing some of its absorbed water once it was removed from the immersion environment. The locus of failure of the degraded samples generally changes to the metal-primer interface. XPS analysis of spots commonly found on failure surfaces following long exposures revealed Fe, indicating the onset of corrosion of the substrate.

Each free standing paint specimen gained weight upon exposure; 1% gain after 8 hours and 2.0-2.5% after 5 days. For longer exposures (up to 4 weeks), samples in the acidic solutions exhibited smaller weight gains (approx. 1.5%) while the samples immersed in distilled water continued to slowly gain weight (to approx. 3%). All of the samples begin to lose some of the gained weight after 8 weeks of exposure presumably due to leaching of the paint/primer constituents.

B) Chamber Exposures

Chamber exposures of alkyd painted steel coupons to 1-ppm SO_2 with an air flow of 60 l/min at a relative humidity of 95% were conducted. Control experiments without SO_2 were also performed. (Some coupons had previously been exposed to ultraviolet radiation by Sam Williams of the Forest Products Laboratory in a Weather-o-meter.) Samples were either kept at a constant temperature (20-23°C) for dry deposition or were thermally cycled (alternating 12h periods at 25-28°C and 15-18°C) for both wet and dry deposition during the exposures. The samples were removed at various time intervals (in the middle of the dry cycle). Samples designed for in-situ EIS monitoring were also included in the latter experiments. It should be noted that all chamber exposed samples except those for in-situ EIS monitoring during the chamber run contain two layers of topcoat on both sides of the sample. The in-situ EIS samples contain a single layer of topcoat on the front side of the specimen. Supplemental information regarding early chamber exposures has been previously detailed (7).

Weight-loss/gain measurements showed that all samples gained weight during the exposure due principally to uptake of water. The majority of the weight gain occurred within the first few days of exposure with little additional increases during the remainder of the 28 day exposure time (Fig. 5). The samples exposed to the diurnal cycle gained ~30-40% more weight than the constant-temperature samples. The fact that the constant-temperature samples increase in weight suggests that moisture is absorbed, although they are not noticeably wet during the dew cycle or when removed from the chamber. No significant difference in the weight gain is seen between samples pre-exposed to UV or not.

As the samples were removed from the environmental chamber, some blistering occurred on the samples used in the final chamber studies (these were the samples with the dry film thicknesses of 120-170 μm). Since these samples were, on average, the thinnest of all the samples examined, the occurrence of blistering was likely related to coating thickness. In addition, after ambient laboratory storage for a few days, brown spots appeared on all (independent of thickness) the SO_2, dew exposed samples that were mounted horizontally (with the top surface exposed). The discoloration is likely an example of a synergistic effect between condensed moisture and SO_2. The brown spots appeared after removal from the chamber only on specimens with condensed dew that were mounted horizontally. We attribute this discoloration to a moisture-induced reaction with the adsorbed S whose local concentration has been increased as a result of the evaporation of condensed dew. When dew forms, the SO_2 adsorbed on the surface or absorbed in the moisture forms H_2SO_3 initially and H_2SO_4 after atmospheric oxidation. On specimens that are mounted vertically, the dew drips off and removes much of the S from the paint surface. However, on horizontal surfaces, not only does the S remain on the surface, but as the dew evaporates during the dry cycle, parts of the surface dry first with the S concentrating in the remaining wet areas. The H_2SO_3 or H_2SO_4 penetrates into the top coat and reacts with the polymer. Nonetheless, the discoloration does not occur until the absorbed moisture, as indicated by the weight gain of each specimen, is lost after a few days in the desiccator.

The effects of SO_2 on samples containing defects was evaluated by scribing some samples diagonally across the front side of the specimen prior to chamber exposure (ASTM D-1654). Scribed samples were exposed in both control and SO_2 chamber studies and were evaluated at the end of the 28 day exposure period. The appearance of the scribed samples after 28 days exposure in the presence and absence of SO_2 is shown in Figure 6. Significant base metal attack with blistering of the adjacent paint was observed for the

horizontally (top) oriented diurnal specimens exposed to SO_2. A close-up view of one of these samples is presented in Figure 7. The corrosion of the vertically oriented diurnal specimens exposed to SO_2 was less severe, however, numerous blisters were observed adjacent to the scribe (Figures 6 and 8). A comparison of the extent of attack as a function of orientation in the chamber during exposure, horizontal (top) or vertical (side), is presented in Figure 8. The nominally dry specimens (not dew-cycled) exposed to SO_2 showed only light rusting along the scribe and no undercutting or blistering adjacent to the scribe. In contrast to the SO_2 diurnal exposures, only light rusting along the scribe was observed for the diurnal specimens exposed during the control run (Figure 6). The paint in the lower left hand corner of one of these specimens was chipped prior to the start of the test and moderate rusting of the base metal was noted in this region. The base metal attack was more severe in this area than along the scribe because moisture tends to accumulate and remain longer at the edges of the specimens (Figure 6). Intermittent areas of very light rust were noted along the scribe of the nominally dry specimens exposed during the control run (Figure 6).

XPS measurements show that all the nominally dry samples adsorbed SO_2 from the test atmosphere (Fig. 9). As one would expect, no S was detected on paint surfaces exposed only to high humidity (control run). The rate of adsorption was greatest initially with 1-2 at.% S present on the surfaces after the first few days; the S concentration subsequently takes the remainder of the 28-day period to approximately double. There is no orientation dependence, but samples that were pre-exposed to UV exhibit ~70% greater uptake of S than samples that were not pre-exposed. High-resolution XPS spectra indicate that the S is in the form of a sulfate.

The results from the samples exposed to dew are very different (Fig. 10). First, there is a strong orientation dependence - samples that were mounted vertically exhibit very little S adsorption (<0.5 at.%) whereas samples that were mounted horizontally exhibit up to 4 at.% S adsorption. Second, the amount of S adsorption on the horizontal samples varies greatly across the surface - the brown areas on horizontally mounted samples have high S concentrations (comparable to that of the dry samples), white areas have significantly less than brown areas, but have higher S uptake than the samples that were mounted vertically. In contrast to the dry samples, no difference was observed between samples pre-exposed to UV and those that were not. Again, the S was in the form of a sulfate.

XPS measurements on brown areas after they were scraped by an Exacto knife and partially removed indicate that S is present throughout the brown spots, but not in the white paint below them. Similar measurements on white areas detected only trace amounts of S both before and after scraping.

The tensile adhesion tests indicate a degradation of the mechanical properties of the paint system during the chamber exposures. Initially, the tensile strength is high (5-6 MPa) with the failure occurring cohesively in either the primer or the top coat. However, upon exposure to SO_2, the strength decreases, until the average value is approximately one-third of the initial value (Fig. 11). Concurrent with this weakening of the paint system is a shift of the locus of failure from within the paint system to the primer metal interface (Fig. 12). Neither UV pre-exposure nor dew exposure during the run was found to have any effect on the degradation of cohesive strength or the loss of adhesion between the primer and the steel - all specimens behaved similarly.

The mechanical properties of the paint system also degrade during the control run, but at a slower rate. SO_2-exposed samples exhibited a significant loss in strength even after exposures as short as one day. (Fig. 11). Even though there was more variation in control samples (Fig. 11), strength losses occurred much more gradually over the 28 day period and final strength values were higher than those witnessed for SO_2 exposure. It is expected that the larger variation witnessed in the control runs is a real, reproducible, effect that is at least partially due to the less aggressive environment in the absence of SO_2. The factors controlling degradation in such an environment are not well defined. On the other hand during SO_2 exposures, degradation is felt to be dominated by SO_2-induced reaction/degradation which is expected to reduce the scatter in the data, since the mechanism and extent of degradation are defined by a single set of reaction kinetics and equilibria.

Figure 12 presents the relationship of tensile adhesion strength with percent of failure occurring at the metal/primer interface for specimens that were chamber exposed in the presence or absence of SO_2. Included in this plot are data from samples that were not tested immediately (within a few hours) after

removal from the chamber, but were allowed to partially "dry" for a few days prior to testing. The relationship between locus of failure and strength remains constant regardless of these variations in test method or exposure condition. As the specimens are exposed in the chamber, the tensile strength decreases significantly and the locus of failure shifts from within the polymer system to the metal/primer interface. The approximately linear relationship of Fig. 12 suggests that the decrease in tensile strength is dominated by a loss or weakening of adhesion between the substrate and the primer and that any reduction in the cohesive strength of the paint system plays a secondary role. This mechanism of failure appears to be the same with and without the presence of SO_2, but SO_2 increases the rate at which the de-adhesion occurs.

In both cases (with and without SO_2) this loss of adhesion is at least partially reversible. When samples that had been stored in a desiccator for several months following exposure were tested, their tensile strengths were close to that of the unexposed specimens.

Although the discoloration is an aesthetic manifestation of SO_2 - induced damage, the decrease in the cohesive strength and adhesion to the metal limits the coatings ability to protect the metal, especially when subjected to stresses caused by thermal cycling or to physical distress, such as abrasion, impact, cutting, etc. This loss of strength also occurs when water alone is present, but the rate of strength loss is enhanced by the presence of SO_2. Before exposure, the adhesion to the steel is strong and failure occurs within the paint system. The fact that the initial measured coating tensile strength is very similar regardless of where the failure occurs (within the top coat, within the primer, or between the top coat and the primer) indicates that the two components have very similar cohesive strengths and that the locus of failure of a particular specimen may depend on slight variations of cure, coating thickness, etc.

Figure 13 presents EIS data for a sample containing the ATMEIS monitor as a function of exposure time in the atmospheric chamber to 1ppm SO_2, 95% RH, with thermal cycling. The quality of the EIS data as well as the expected decrease in low frequency impedance with exposure time demonstrates the feasibility of the monitor for studying and evaluating coating degradation in atmospheric exposures. Figure 14 compares near DC resistance values as a function of exposure time for ATMEIS specimens during the SO_2 experiment with tensile adhesion strength measurements for a series of conventional specimens (samples which do not contain the ATMEIS monitor, but are otherwise nominally identical) exposed during the same chamber run. Decreases in near DC impedance correspond well to changes in the mechanical properties. ATMEIS data are given for two different samples and tensile adhesion values are averages of at least 3 specimens. Locus of failure in the tensile specimens occurs initially within the paint system, but shifts to the metal primer interface at later exposure times. Visual examination of the failure surface indicates that this failure is associated with corrosion at the metal/primer interface. Thus, EIS is detecting corrosion at the interface.

Figure 15 compares EIS data for the ATMEIS during exposure to SO_2, 95% RH to data for exposure in the atmospheric exposure chamber under the same conditions, but in the absence of SO_2. Although these data only represent a comparison of two chamber runs, the data are suggestive of enhanced degradation of the coating in the presence of SO_2. It further indicates the sensitivity of the monitor in indicating degradation. The changes detected during the chamber run clearly demonstrate the feasibility of the ATMEIS monitor for atmospheric monitoring. Further, these changes are consistent with the changes in the mechanical integrity of the coating system.

One unexpected observation was low initial low frequency impedance data for the chamber exposed ATMEIS. Initial low frequency values for specimens with the ATMEIS ranged from 10^{11} to 10^{9} ohms in immersion exposure. Initial low frequency values for specimens with the ATMEIS in chamber exposure ranged from 10^{8} to 10^{7} ohms. This behavior is possibly due to the existence of pinhole defects at the sample edges which would not be exposed in the immersion exposures used to preliminarily evaluate these samples. Another possibility is additional porosity of the coatings used in chamber exposures. Chamber exposed ATMEIS specimens contained only a single layer of topcoat compared to most other specimens which contained two layers of topcoat. A single topcoat layer is expected to be more porous than a double layer and, therefore, some decrease in the impedance is predicted. In separate immersion studies with the edges of the specimens unexposed, the effect of single vs double coat specimens in influencing impedance values was found to be much less (~1 order of magnitude difference) than the low impedance values (~3-4 orders of magnitude difference) witnessed during chamber exposure of ATMEIS specimens. In addition, the low

impedance values in chamber exposures are only approximately an order of magnitude higher than those witnessed at early times for complete immersion (with the edges exposed) in aqueous acids. This provides support that the behavior is related to defects at the edges of the specimens which was further validated by the following measurements. EIS data were collected for samples prior to chamber exposure which were wetted taking care to prevent the edges from receiving appreciable moisture. Samples were then re-sprayed to ensure that the edges of the sample were wetted (but not immersed). A significant drop in the near DC impedance was witnessed after the more complete exposure to water indicating that low impedance pathways existing at the edges of these samples may contribute significantly to impedance behavior during chamber exposure.

This phenomenon also indicates that the monitor can detect defects in areas other than those immediately adjacent to the gold electrode. To further evaluate this effect an ATMEIS specimen, exposed via immersion, was intentionally defected to expose ~1-2 mm^2 of the underlying steel substrate between the gold grid lines. EIS data were generated prior to and after the imposition of this intentional defect. A change in the near DC impedance behavior of several orders of magnitude was witnessed, clearly demonstrating the ability of the monitor to detect defects in areas adjacent to the gold electrode. The remote sensing ability of the monitor is likely due to conductivity through the moisture film present on, or within, the coating surface.

The relationship between EIS data obtained with the ATMEIS monitor and tensile adhesion strength for samples exposed to the same environment provides encouragement that EIS data may be used as an indicator of mechanical properties and the changes in these properties due to degradation. Although one other study reports similar effects (8), we are not aware of any studies which have evaluated the extent of this correlation for the same samples. To fully evaluate this effect specimens were immersion exposed to pH 3 H_2SO_4 and EIS data were collected throughout this exposure time. One day after specimens were removed from exposure, tensile adhesion testing was completed. The correlation between tensile adhesion data and near DC impedance measured just prior to removal from exposure is shown in Fig. 16. Although these data are for a limited number of samples (averages of 3-15 samples), the correlation is quite good. Fig. 17 shows the correlation of tensile adhesion strength for these specimens to % metal/primer failure. This correlation is also quite good. As was previously mentioned, the locus of failure in unexposed specimens or after very short exposure times is generally cohesive in the paint system. After longer exposure times this failure shifts to the metal/primer interface and has been associated with corrosion of the interface evaluated visually and with XPS (7). Thus, the fact that strength measurements correlate well with fraction of metal/primer failure and that EIS data correlate well with strength indicates that EIS may be used as a non-destructive means of assessing changes in mechanical properties and extent of corrosion at the metal/primer interface.

SECTION 5

CONCLUSIONS

1) An accelerated curing process which is reproducible and results in near full cure for single and double coat specimens has been adopted.
2) Specific analytical techniques capable of detection of coating degradation at early exposure times have been either identified or developed. A good correlation exists between non-destructive electrochemical (EIS) and mechanical test methods indicating new possibilities for evaluation of coating degradation.
3) Under aqueous conditions S penetrates the paint film upon exposure to sulfurous acid, but does not penetrate the film upon exposure to sulfuric acid. In addition, the presence of water, in immersion exposures, overrides the effects of the individual pollutants.
4) Exposure to 1 ppm SO_2 at 95% RH causes significantly more deterioration of coated metal substrates over exposure to 95% RH in the absence of SO_2. This deterioration is manifested as localized discoloration, damage at defects, and changes in tensile adhesive strength and locus of failure in chamber exposed samples as a function of exposure time. These discolored regions which occur only on samples on which dew condensed and was allowed to dry are areas of high S concentration. Significant blistering and rusting occurred on samples containing intentional defects. This damage was most severe for samples that were dew cycled and mounted horizontally during chamber exposure.
5) Data from chamber exposed samples incorporating the ATMEIS electrochemical monitor also indicates coating deterioration as a function of exposure time to 1ppm SO_2 at 95% RH with diurnal cycling.
6) Pre-exposure of samples to UV and/or diurnal cycling (during exposure) can effect the severity of this degradation as indicated by the discoloration and the amount of S detected on the surface.

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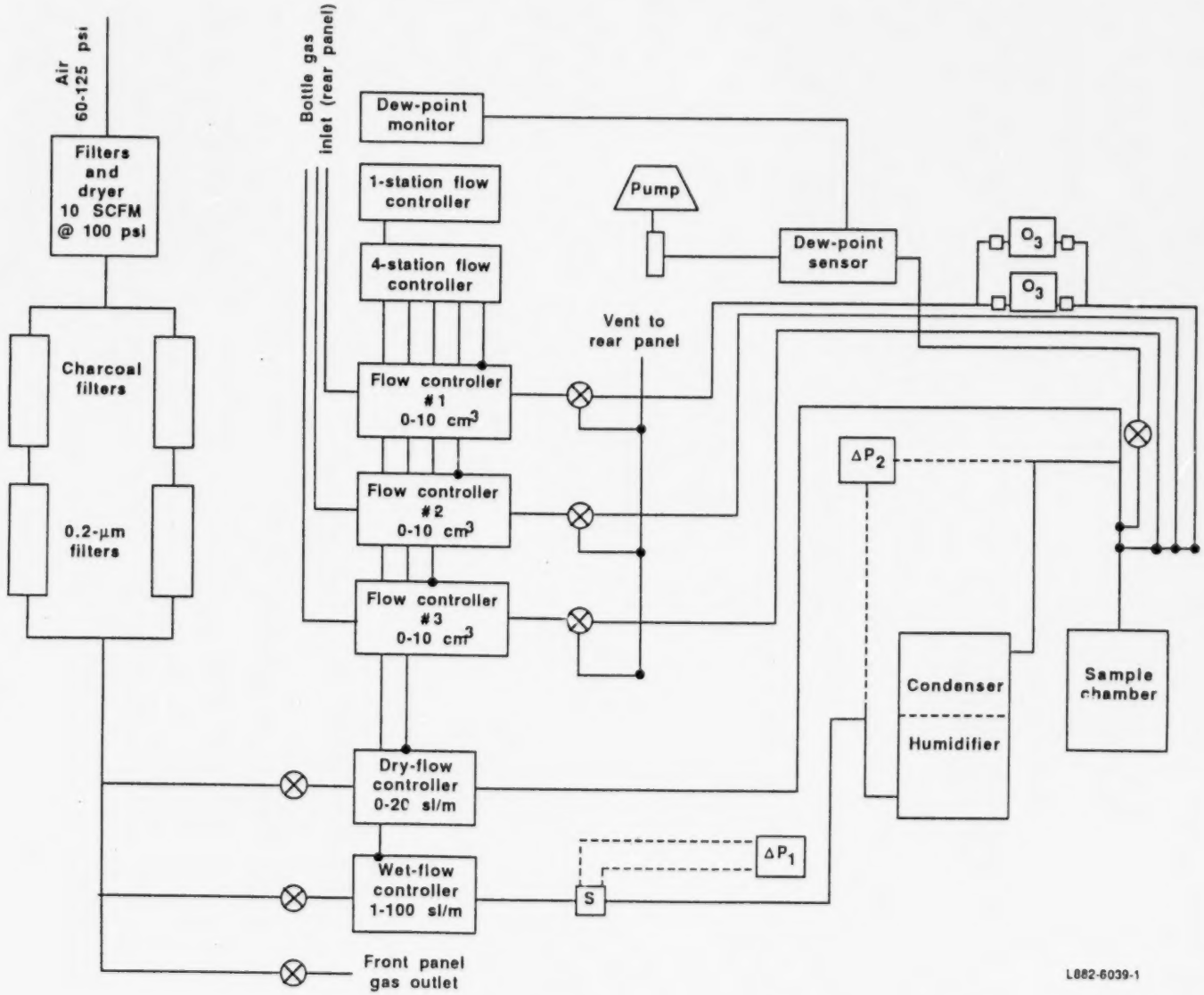

Figure 1 Schematic diagram of the environmental exposure chamber.

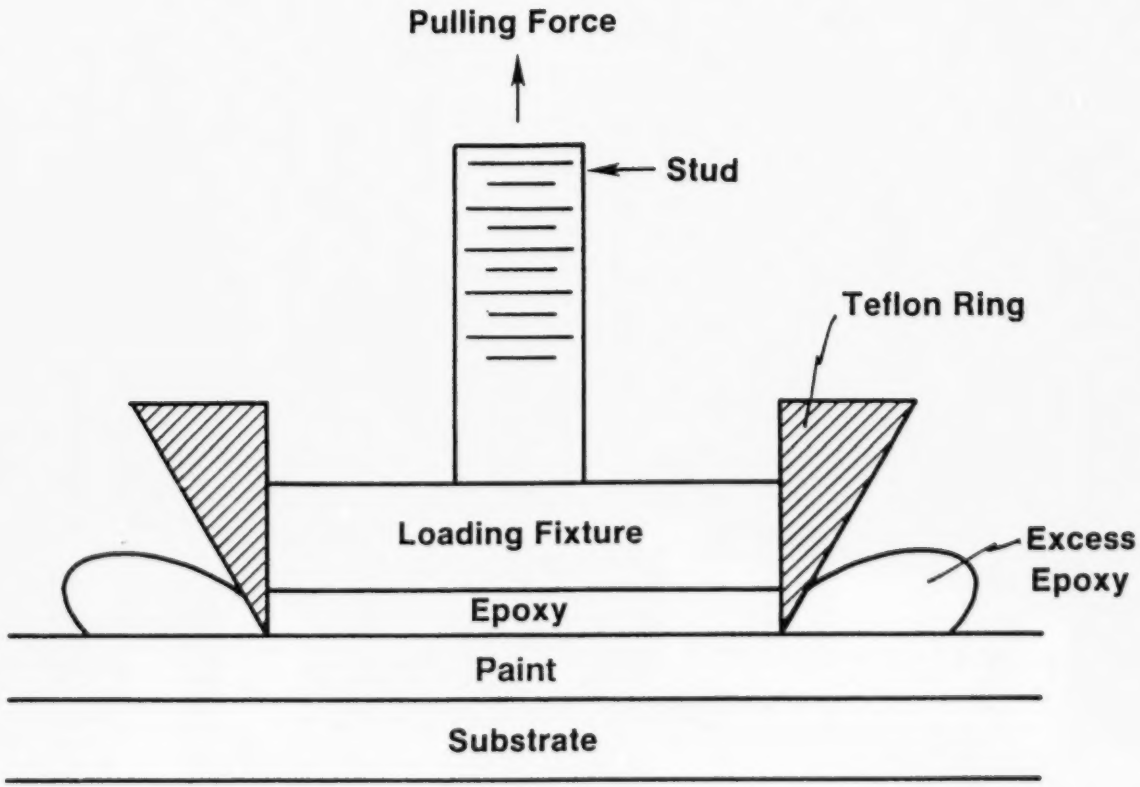

Figure 2 Schematic diagram of the tensile adhesion test method.

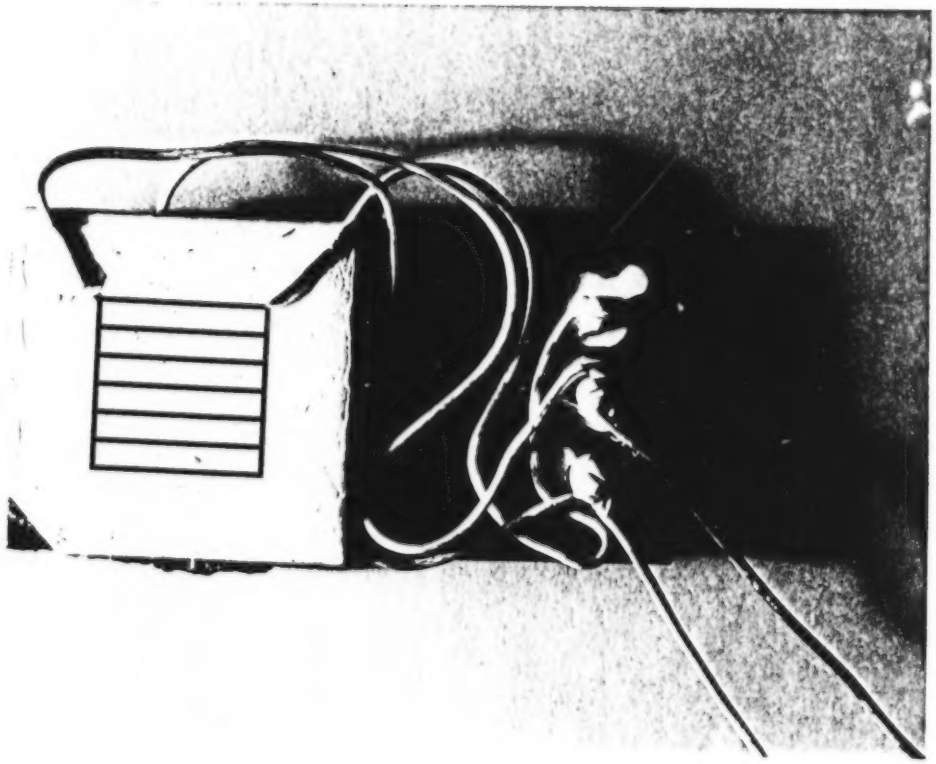

Figure 3 Picture of the ATMEIS monitor, mounted for chamber exposure. In immersion exposures only the central portion of the 2.54 cm x 2.54 cm coupon (portion which contains the gold grid electrode) would be exposed.

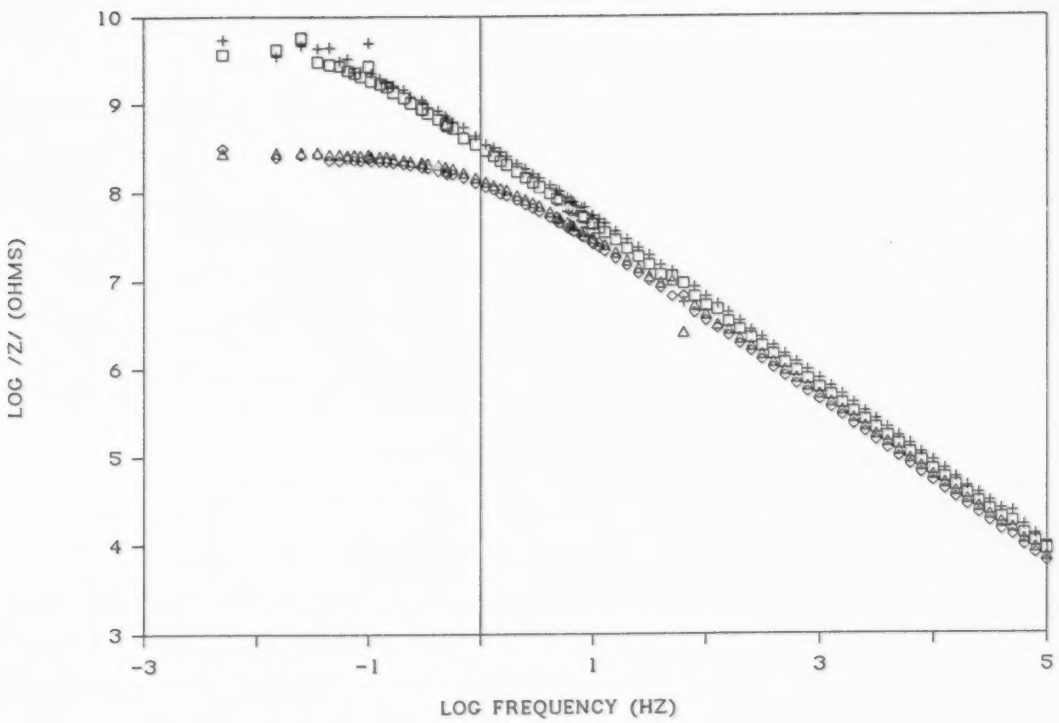

Figure 4 Bode magnitude plot of EIS data for the ATMEIS monitor collected using remote reference/counter electrodes (+, △) or the gold electrode as reference/counter with the aqueous electrolyte removed (□, ◇) after 1 day, two weeks exposure to aerated, pH 3, H_2SO_4.

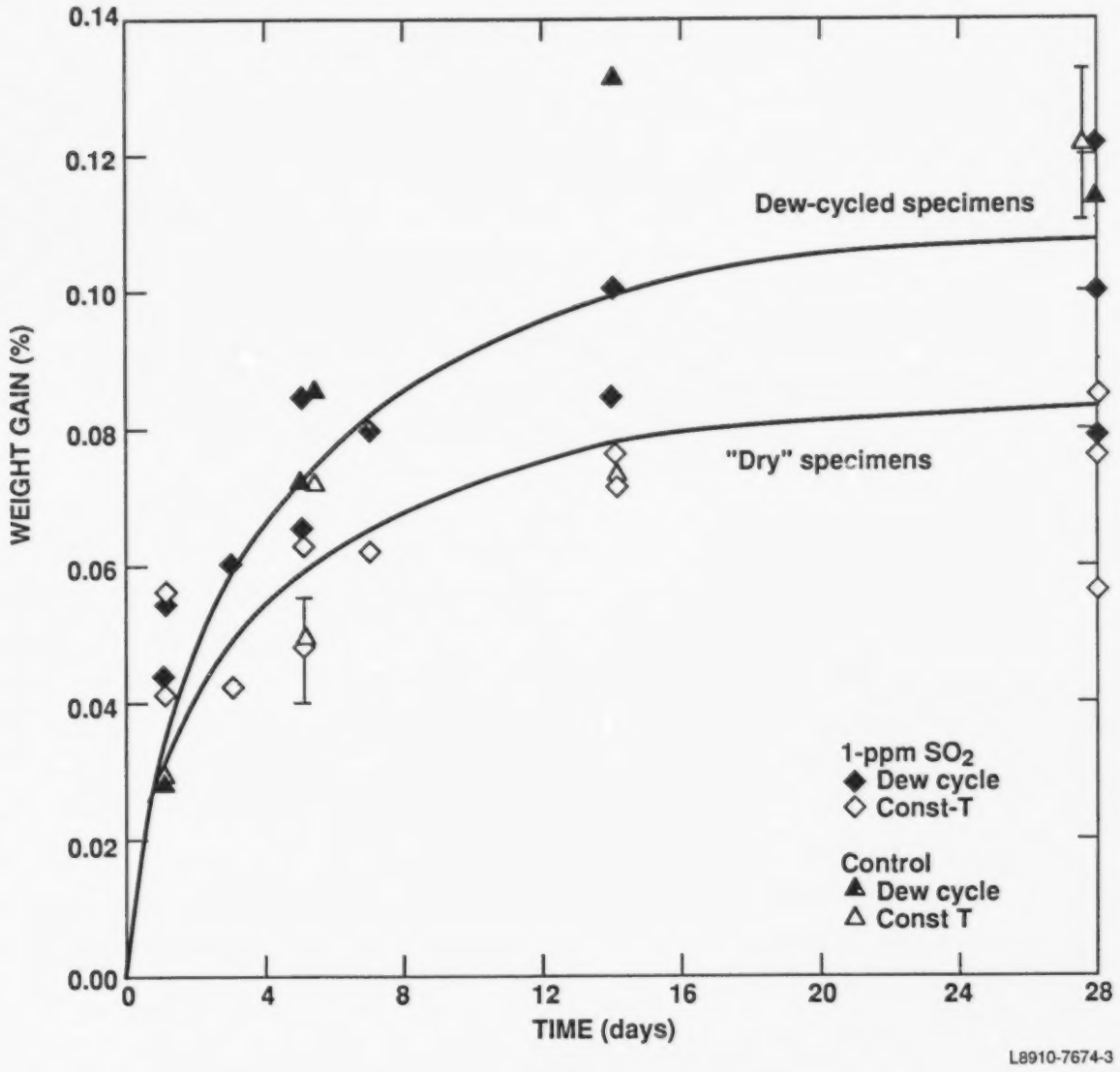

Figure 5 Weight gain for chamber exposed specimens as a function of time for samples exposed to 1 ppm SO_2. Typical standard deviations are shown.

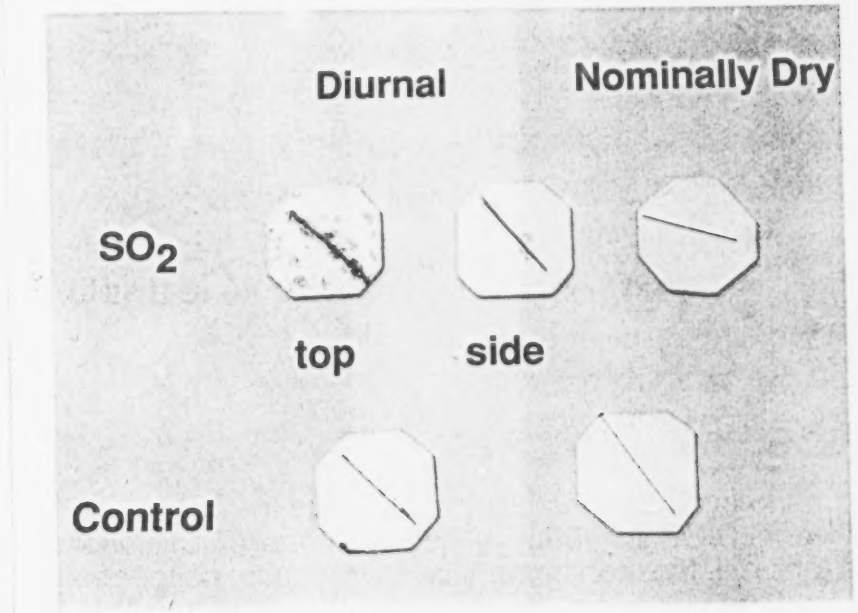

Figure 6 Comparison of scribed samples after 28 days chamber exposure in the presence (SO_2) and absence (Control) of SO_2. The differences in extent of degradation for specimens mounted horizontally (Top) and vertically (Side) and dew temperature cycled (Diurnal) or constant temperature (Nominally Dry) is also compared.

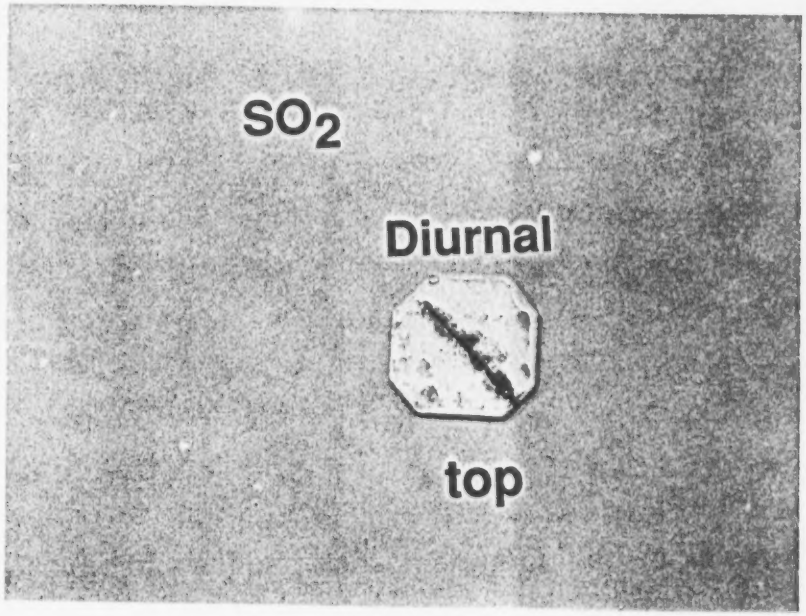

Figure 7 Picture of a scribed horizontally mounted sample after 28 days of diurnal temperature cycled chamber exposure to 1ppm SO_2.

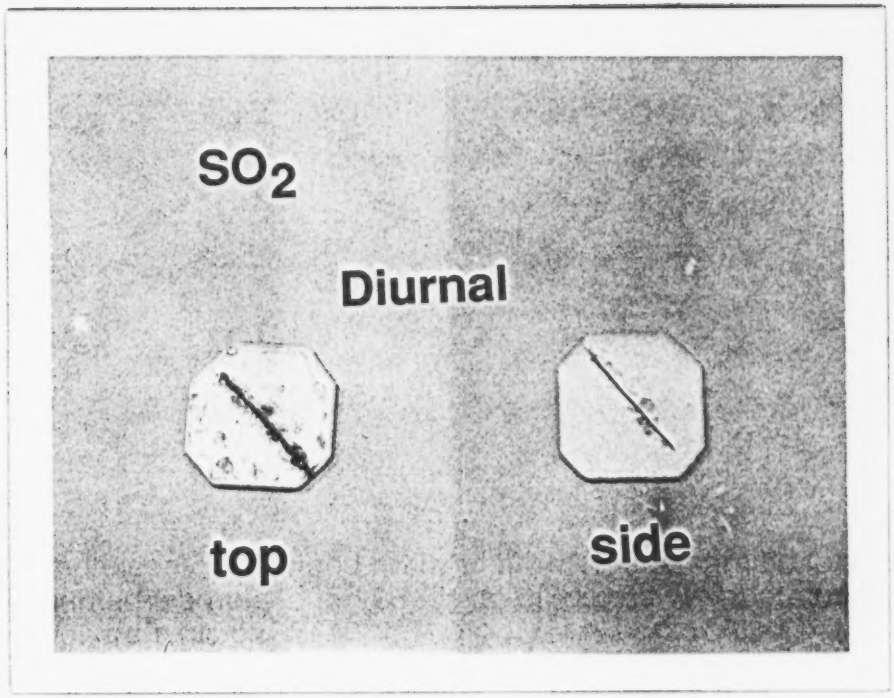

Figure 8 Comparison of a scribed horizontally mounted sample to a scribed vertically mounted sample after 28 days of diurnal temperature cycled chamber exposure to 1ppm SO_2.

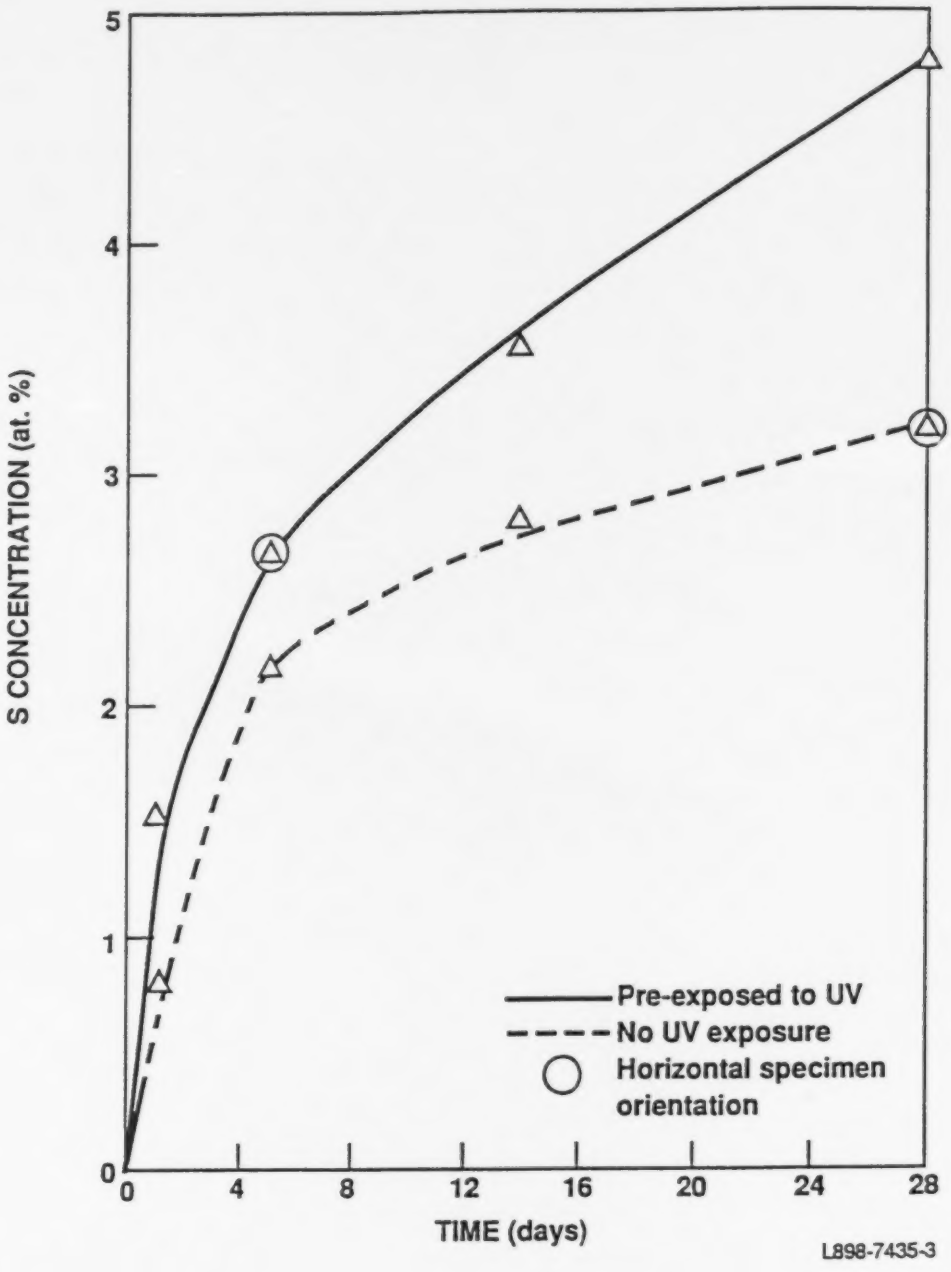

Figure 9 Plot of rate of S uptake as a function of SO_2 exposure time in the atmospheric chamber for nominally dry samples. The top curve corresponds to samples pre-exposed to UV; the bottom curve to those that were not.

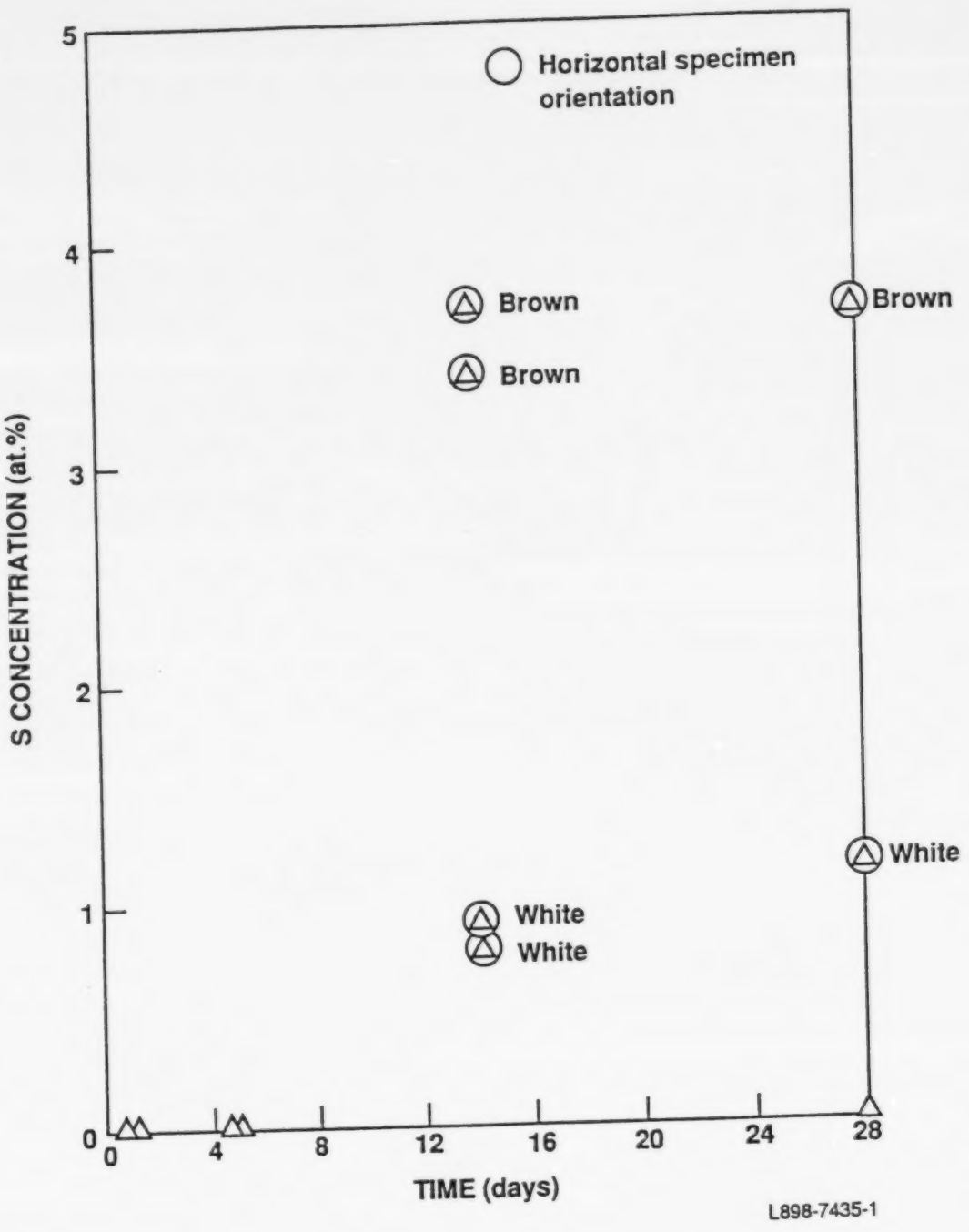

Figure 10 S concentration, as measured by XPS, as a function of SO_2 exposure time in the atmospheric chamber for dew-cycled samples.

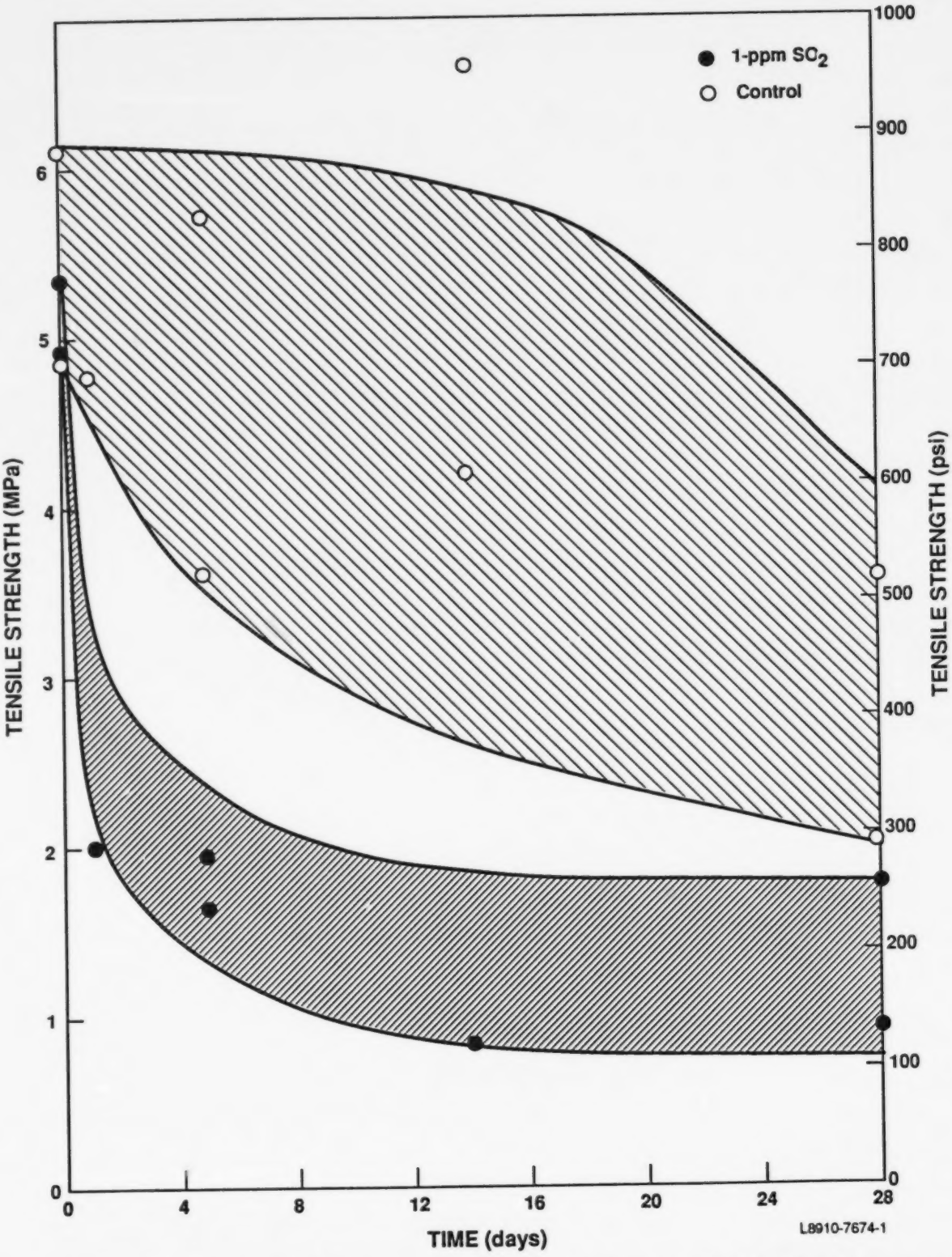

Figure 11 Tensile adhesion strength as a function of chamber exposure time. No significant difference was seen between the dry and dew-cycled samples or between the UV-exposed and not exposed samples; consequently, the data have been averages over all conditions for each run. Shading reflects run-to-run variation.

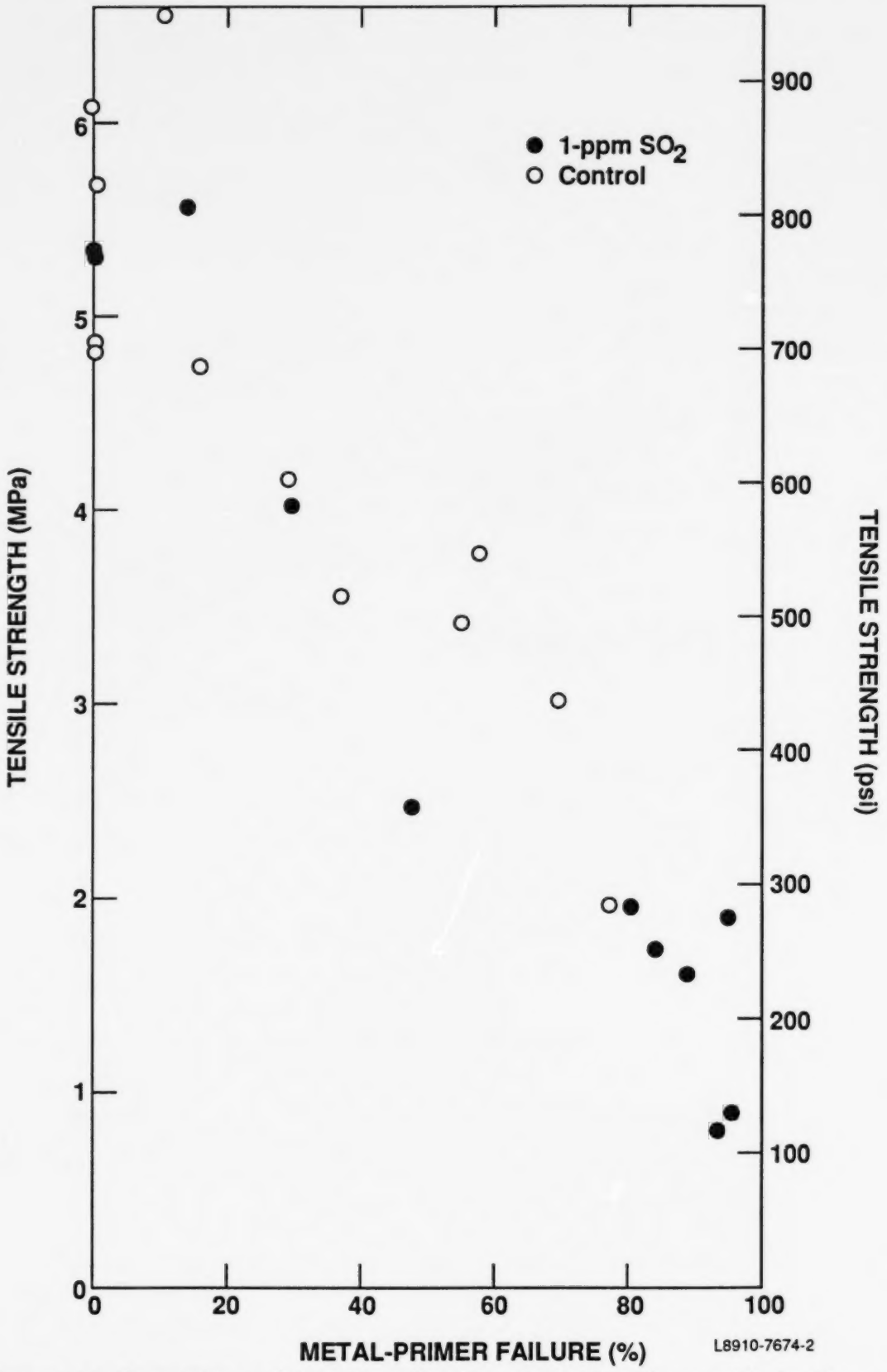

Figure 12 Correlation of tensile adhesion strength values with fraction of failure occurring at the metal-primer interface. Data have been averaged over all conditions and include some specimens that were tested after a hold time to allow partial drying.

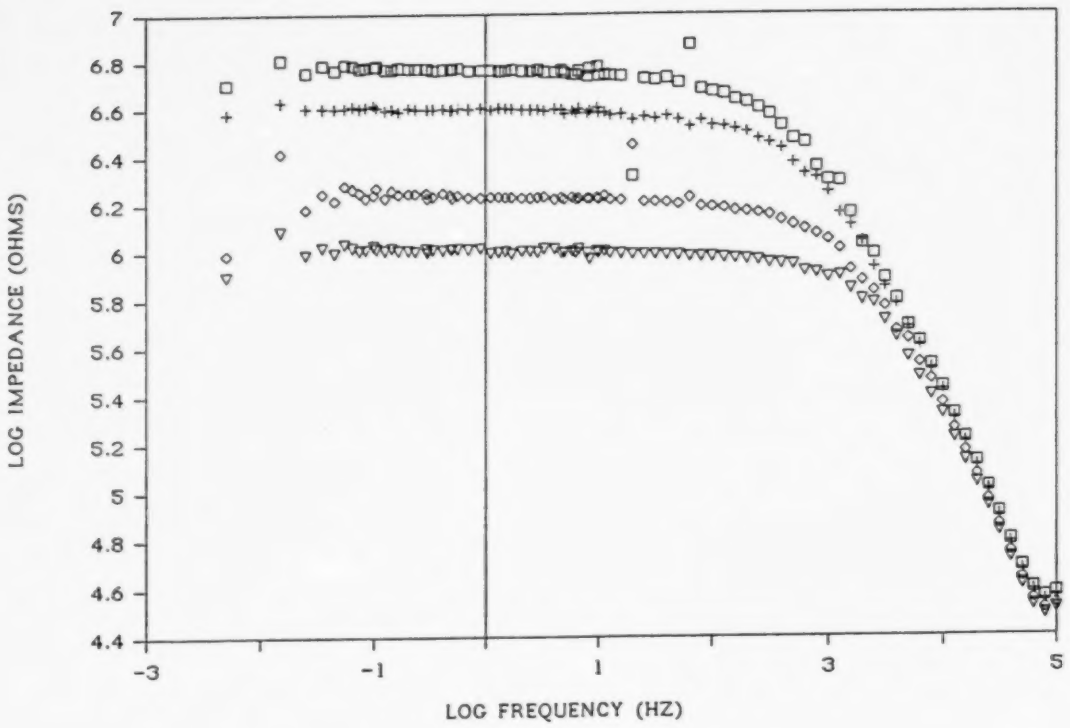

Figure 13 EIS data, plotted in the Bode magnitude format, for an ATMEIS monitor after 2 (□), 5 (+), 7 (◇), and 19 (▽) days exposure in the atmospheric exposure chamber to 1 ppm SO_2, 95% RH.

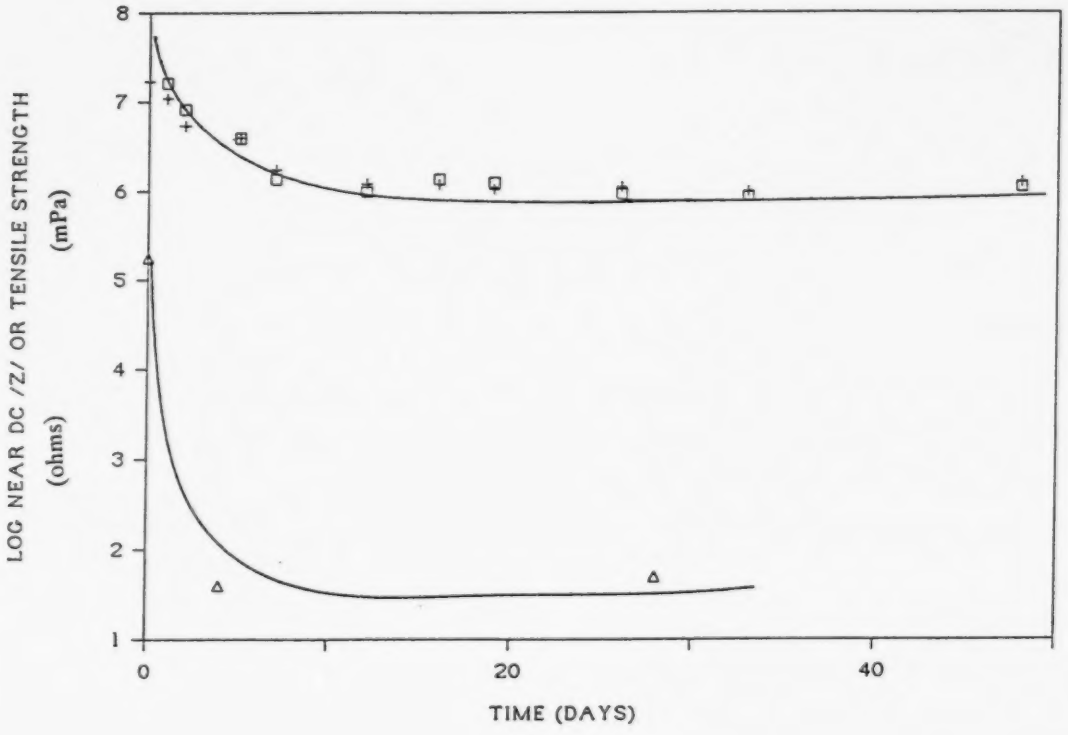

Figure 14 Comparison of near DC impedance values (~5-20 mHz) for two ATMEIS monitor specimens (+,□) to average tensile adhesion strength values for conventional specimens (△) as a function of exposure time in the atmospheric exposure chamber to 1 ppm SO_2, 95% RH.

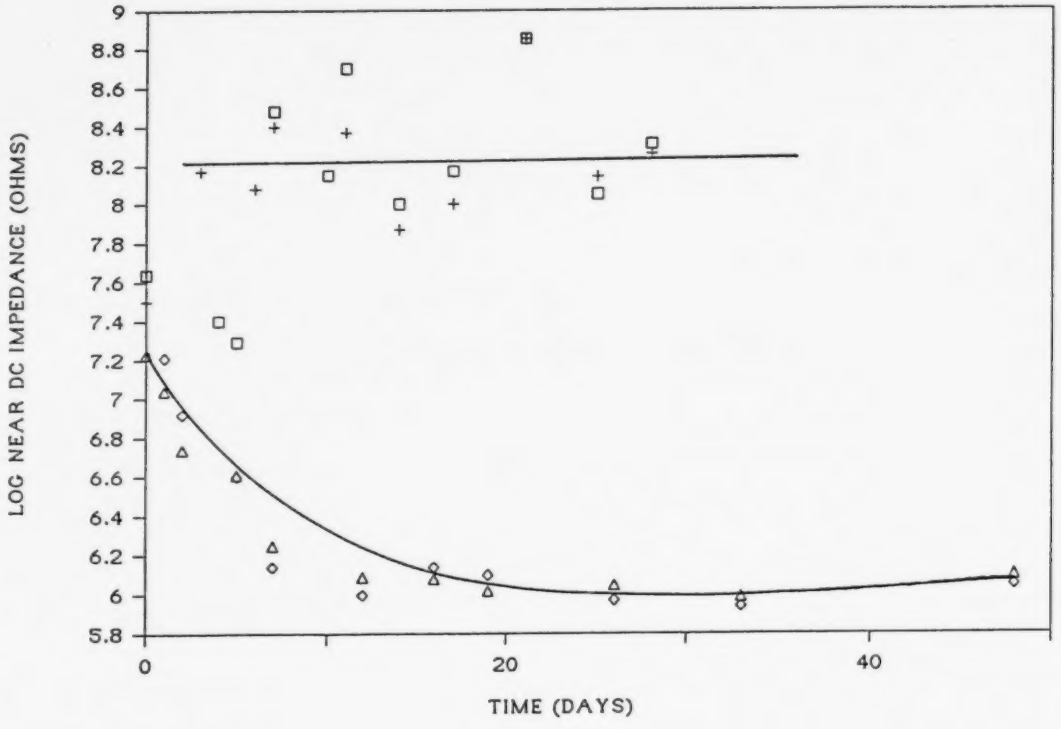

Figure 15 Comparison of near DC impedance values (~5-20 mHz) for two ATMEIS monitor specimens (△,◇) exposed to 1 ppm SO_2, 95% RH to near DC impedance values for two ATMEIS monitor specimens (+, □) exposed to 95% RH as a function of exposure time in the atmospheric exposure chamber.

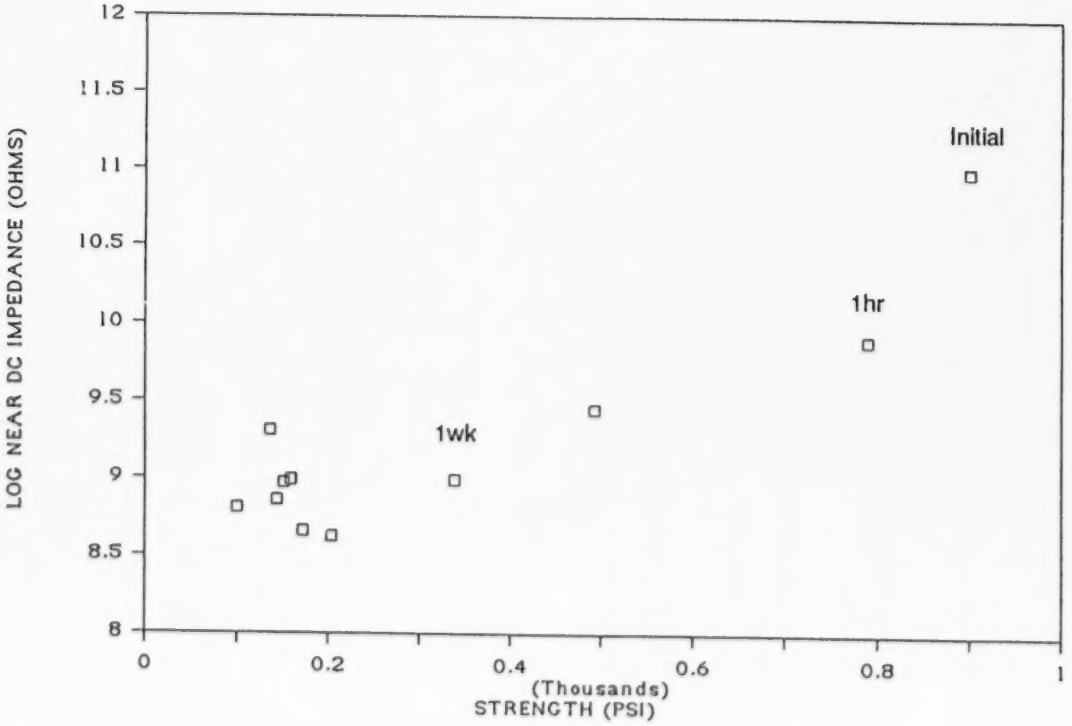

Figure 16 Plot of average near DC impedance values as a function of average tensile adhesion strength for specimens which were immersion exposed in aerated, pH 3, H_2SO_4. EIS data were collected just prior to removal from exposure; tensile adhesion strength was measured on the same samples after removal from exposure. Averages are computed at each exposure time (1 hour to several weeks).

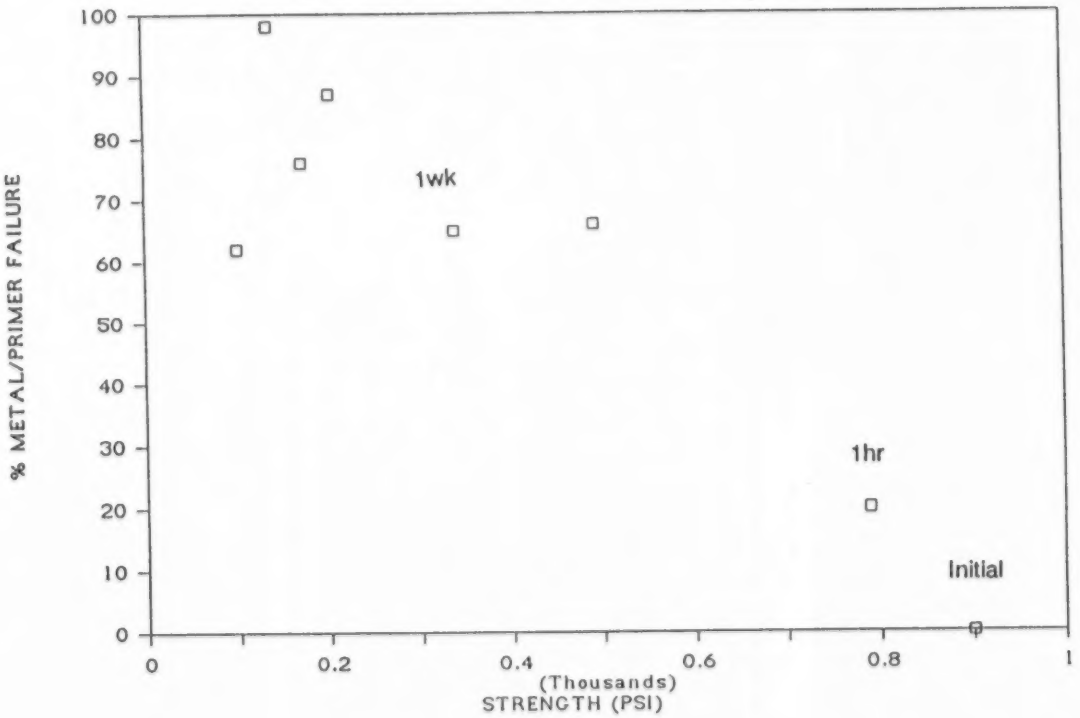

Figure 17 Plot of average tensile adhesion strength as a function of average % metal/primer failure for specimens which were immersion exposed in aerated, pH 3, H_2SO_4. % Metal/primer failure was evaluated visually. Averages are computed at each exposure time (1 hour to several weeks).